Catalytic Analysis. XIV : Rapid Microdetermination of Sulfide, Thiosulfate and Thiocyanate by Gas Evolution Method

Catalytic Analysis. XIV
Rapid Microdetermination of Sulfide, Thiosulfate and Thiocyanate by Gas Evolution Method*

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Synopsis

In iodine-azide reaction catalysed with sulfide, thiosulfate and thiocyanate, the volume of nitrogen gas evolved in a definite period of time was found to be linear against the amount of the catalysers. By means of Lunge's nitrometer 20~160γ of sulfide and thiocyanate and 50~200γ of thiosulfate could be determined in a few minutes.

I. Introduction

In the preceding papers some microdeterminations were made by measuring the velocity of some developing or fading reactions of color when catalysed with microamounts of substances. In these cases, the definite relations were found between the amount of the catalyser and the reaction velocity, which made the microdeterminations of catalysers possible. If the catalysed reaction would be accompanied with an evolution of some kind of gas, it should be possible to determine the microamounts of catalyser by utilizing the relation between the amounts of the catalyser and the velocity of the gas evolution.

Nitrogen gas was evolved in the iodine-azide reaction[1] catalysed with sulfide, thiosulfate and thiocyanate, which were employed in Catalytic Analysis V[2] by the use of some fluorescense indicators. Therefore, the microdeterminations of sulfide, thiosulfate and thiocyanate seem to be possible by measuring the volume of nitrogen gas evolved in a definite period of time.

II. Experimental results

1. Experimental procedure

A small glass crucible containing the catalyser solution was floated in the

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reaction vessel of Lunge's nitrometer which contained iodine, azide and other reagent solutions. When they were mixed by shaking, the gas was evolved, the volume of which was read on the scale of the nitrometer after a definite period of time. Temperature was 15~20°, and the corrections for the temperature and the pressure of atmosphere were not made.

2. Determination of sulfide

(1) Concentration of reagents

Sodium salt of sulfide was used and a suitable concentration of reagents was examined for the most sensitive reaction. After the measurements of the gas evolution velocity at various concentrations of reagents in 20 ml of total volume, it was found that the use of 3.5 ml of 3% sodium azide, 2.0 ml or more of 0.5N iodine and 0.4~0.6 ml of 0.1N acetic acid were suitable for the most sensitive evolution of nitrogen gas.

(2) Gas evolution velocity and amount of sulfide

Under the most sensitive condition found in the above experiment, the gas evolution velocity was measured with various amounts of sulfide which were separately added in 20 ml of total solution containing 3.5 ml of 3% sodium azide, 0.4 ml of 0.1N acetic acid and 2.0 ml of 0.5N iodine.

Gas evolution could not be recognized without sulfide. The volumes of nitrogen gas evolved in a definite period of time after mixing were read on the nitrometer and are tabulated in Table 1. The gas evolution was rather violent within the first two minutes, but, after that it became stationary.

Table 1. Gas evolution velocity and amount of sulfide.

Amount of sulfide (γ)	Volumes of nitrogen gas evolved (Mean of twice) (ml)							
	15(sec)	30(sec)	1(min)	2(min)	4(min)	4(min)	5(min)	10(min)
20	1.5	2.0	2.4	2.7	3.0	3.3	3.5	4.5
40	2.4	2.9	3.4	3.7	4.0	4.2	4.4	5.3
60	3.1	3.7	4.4	4.7	4.9	5.1	5.3	6.3
80	4.2	4.7	5.2	5.6	5.9	6.2	6.4	7.2
100	5.0	5.8	6.4	6.8	7.0	7.2	7.4	8.2
120	5.7	6.5	7.0	7.4	7.6	7.8	8.0	9.0
140	6.2	7.2	7.9	8.3	8.6	8.8	9.0	10.1
160	7.5	8.4	8.9	9.4	9.7	9.9	10.1	11.1

The gas volumes in 2, 5 and 10 minutes after mixing were plotted against the amount of sulfide as shown in Fig. 1.

The relations obtained are all linear. Therefore, the determination of 20~160γ of sulfide can be made by measuring the volumes of nitrogen gas evolved in

(1) F. Rashig, Ber., **48** (1915), 2088.
(2) H. Gotō and T. Shiokawa, Sci. Rep. RITU, A, **1** (1949), 41.

2, 5 or 10 minutes after mixing under the same condition, and especially if the relation at 2 minutes could be obtained, the microdetermination of sulfide may be made very rapidly within about five minutes.

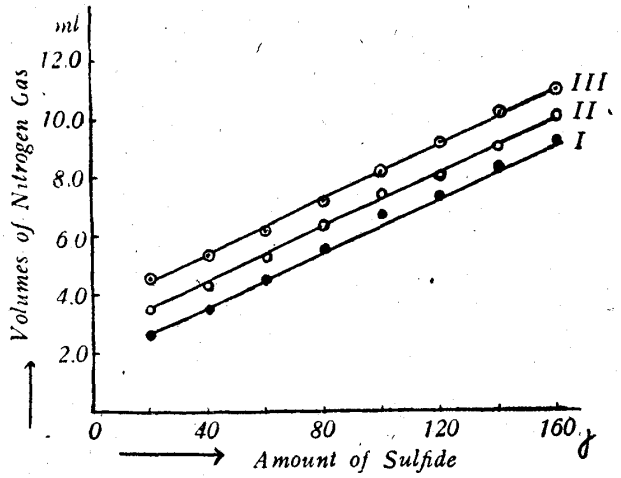

Fig. 1 Volumes of nitrogen gas and amount of sulfide

I: for two minutes
II: for five minutes
III: for ten minutes

3. Determination of thiosulfate

(1) Concentrations of reagents

Sodium salt of thiosulfate was used and a suitable concentration of reagents was examined in the same way as before. The concentration of acetic acid much influenced the catalytic reaction of thiosulfate. The use of 1.0 ml of 0.1N acetic acid in 20 ml of total solution made the reaction most sensitive, and the uses of 3.5 ml of 3% sodium azide and 2 ml of 0.5N iodine were also suitable.

(2) Gas evolution velocity and amount of thiosulfate

Under the most sensitive condition found in the preliminary experiment, the gas evolution velocity was measured in various amounts of thiosulfate, which were added separately in 20 ml of total solution containing 3.5 ml of 3% sodium azide, 1.0 ml of 0.1N acetic acid and 2.0 ml of 0.5N iodine. The volumes of nitrogen gas evolved were read on the nitrometer and the results obtained are tabulated in Table 2.

Table 2. Gas evolution velocity and amount of thiosulfate

Amount of	Volumes of nitrogen gas evolved (Mean of twice) (ml)							
thiosulfate (γ)	15(sec)	30(sec)	1(min)	2(min)	3(min)	4(min)	5(min)	10(min)
50	1.5	1.7	1.9	2.2	2.4	2.5	2.6	3.1
75	2.1	2.4	2.8	3.0	3.1	3.2	3.3	3.6
100	2.8	3.2	3.5	3.7	4.0	4.1	4.2	4.7
125	3.3	3.8	4.1	4.4	4.5	4.5	4.7	5.3
150	4.1	4.4	4.7	5.0	5.1	5.2	5.4	5.9
175	4.3	4.8	5.1	5.3	5.5	5.6	5.7	6.2
200	4.8	5.2	5.5	5.7	5.9	6.0	6.2	7.1

The gas was evolved violently in the same manner as before in the first few

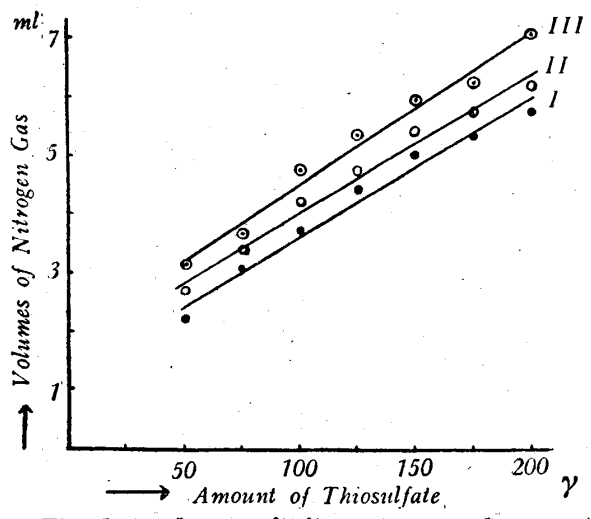

Fig. 2. Volumes of nitrogen gas and amount of thiosulfate

I: for two minutes
II: for five minutes
III: for ten minutes

minutes, and then the evolution became stationary.

The gas volumes in 2, 5 and 10 minutes were plotted against the amount of thiosulfate as shown in Fig. 2.

Applying the linear relations between them, the determination of 50~200γ of thiosulfate can be made by measuring the gas volumes under the same condition, and the quick determination may be made by the relation at 2 minutes as before.

4. Determination of thiocyanate

(1) Concentrations of reagents

Potassium salt of thiocyanate was used and a suitable concentration of reagents was examined in the same way as the preceding experiments. It was desirable that the concentration of acetic acid should be higher than those in the other cases. The use of 3.0~4.0 ml of 0.1N acetic acid in 20 ml of total solution gave most sensitive reaction and the uses of 3.5 ml of 3% sodium azide and 0.5~1.0 ml of 0.5N iodine were also suitable for the purpose.

(2) Gas evolution velocity and amount of thiocyanate

Under the most sensitive condition found in the preliminary experiments, the gas evolution velocity was measured in various amounts of thiocyanate, which were also added separately in 20 ml total solution containing 3.5 ml of 3% sodium azide, 3.0 ml of 0.1N acetic acid and 1.0 ml of 0.5N iodine. The volumes of nitrogen

Table 3. Gas evolution velocity and amount of thiocyanate

Amount of thiocyanate (γ)	Volumes of nitrogen gas evolved (Mean of twice) (ml)							
	15(sec)	30(sec)	1(min)	2(min)	3(min)	4(min)	5(min)	10(min)
20	0.3	0.5	0.8	1.1	1.4	1.6	1.8	2.7
40	0.4	0.6	1.0	1 5	1.9	2.3	2.5	3.8
60	0.5	0.9	1.3	1.9	2.4	2.8	3.2	4.6
80	0.6	1.0	1.6	2.3	2.9	3.5	3.8	5.3
100	0.6	1.1	1.8	2.6	3.3	4.0	4.5	6.2
120	0.6	1 2	2.0	3.0	3.8	4.4	4.9	6.8
140	0.8	1.4	2.2	3.4	4.3	4.9	5.5	7.3
160	1.0	1.6	2.5	3.8	4.6	5.4	5.9	8.3

gas evolved were read on the nitrometer and the results obtained are tabulated in Table 3.

The gas volumes evolved in 2, 5 and 10 minutes were plotted against the amount of thiocyanate as shown in Fig. 3.

Applying the linear relations between them, the determination of 20~160γ of thiocyanate can be made by measuring the gas volumes under the same condition. A rapid determination can be accomplished in the same way as before.

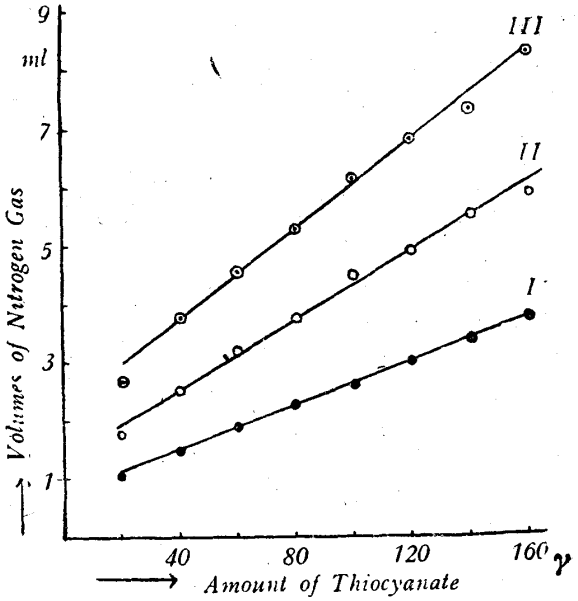

Fig. 3 Volumes of nitrogen gas and amount of thiocyanate

I: for two minutes
II: for five minutes
III: for ten minetes

5. Influences of diverse ions

Influences of some diverse ions on this way of determination were tested by making the same measurements in the presence of chloride (potassium salt), sulfate (sodium salt), nitrate (sodium salt), phosphate (sodium salt), manganese (chloride), chromium (nitrate), ferric iron (sulfate), tartaric acid and citric acid. Chloride, sulfate, nitrate, phosphate and manganese had no influences even in the presence of 10 mg of each, and tartaric and citric acids also had no influences even in the presence of 20 mg of each. Chromium had no influence in the presence of 10 mg in the determination of sulfide and thiocyanate, but the presence of more than a few milligrams interfered in the determination of thiosulfate. Ferric iron had much influence on the determination of sulfide in the presence of more than 0.2 mg and on that of thiosulfate and thiocyanate in the presence of more than a few milligrams.

Summary

(1) Applying the iodine-azide reaction catalysed with sulfide, thiosulfate and thiocyanate, the microdetermination of these ions were studied by measuring nitrogen gas evolved with Lunge's nitrometer.

(2) The suitable concentrations of reagents for the analysis were examined and, under a definite condition it was found that the volumes of nitrogen gas evolved in a definite period of time varied all linear with the amount of these catalysers.

(3) The relations rendered it possible to determine 20~160γ of sulfide and thiocyanate, and 50~200γ of thiosulfate in a few minutes.
(4) Influences of some diverse ions on the determination were examined.

Acknowledgment

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